Solid state studies of some nitrosoaromatic iron carbonyls

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Abstract

Mössbauer spectroscopic studies of a tricarbonyl-(nitrosobenzene)iron compound and two dicarbonyl-(nitrosobenzene)triphenylphosphineiron compounds have shown that these compounds possess similar structures and are dimeric in character. Solid state ^{13}C NMR spectroscopy shows that although in such compounds the NO bond length approaches that characteristic of a single bond, the large *ipso* chemical shift of the NO group is only slightly diminished. Other consequences of coordination for the structure of the C–nitroso ligand are also discussed.

Key words: Iron; Carbonyl; Mössbauer spectra; Nuclear magnetic resonance; Nitroso compound; Phosphine

1. Introduction

Over twenty years ago Barrow and Mills [1] established the crystal and molecular structure of bis [tricarbonyl-(3-chloro-2-methylnitrosobenzene)-iron] (see Fig. 1). This compound was the only one of a series of tricarbonyl–nitrosobenzene iron complexes [2,3] that yielded crystals large enough for a single-crystal X-ray study. Although the colligative properties of these nitrosoaromatic iron tricarbonyls suggested that both monomeric and dimeric forms existed in solution in a ratio depending upon the substitution in the ring of the nitrosobenzene, most other physical properties of the complexes suggested that structurally they were similar. A crucial piece of evidence was provided by Frank and Bunbury [4], whose Mössbauer spectroscopic studies demonstrated that the structures of four nitrosoaromatic iron tricarbonyls were the same although the molecular weights determined by osmometry implied that two of the compounds were dimeric, one monomeric, and the degree of association of the fourth was 1.4 [3].

The availability of solid state ^{13}C NMR spectroscopy suggested that additional evidence for the structure of these solid complexes could be obtained. A further complex is known to be formed when triphenylphosphine reacts with bis[tricarbonyl(nitrosobenzene)iron] and this compound, triphenylphosphinedicarbonyl-(nitrosobenzene)iron was considered to be monomeric on the basis of cryoscopic measurements [2]. It seemed appropriate to extend the NMR and Mössbauer studies to these complexes in order to provide a basis for understanding their structure in the solid state.

2. Experimental details

Bis[tricarbonyl(nitrosobenzene)iron] and bis[tricarbonyl(4-methyl-nitrosobenzene)iron] were prepared by the previously described method [2,3] involving u.v. photolysis of the nitroarene with iron pentacarbonyl.

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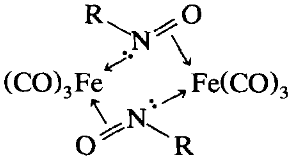

Fig. 1. Bis [tricarbonyl-(3-chloro-2-methylnitrosobenzene)-iron].

The melting point and IR spectra agreed with the published data. Reaction of the above compounds with triphenylphosphine was carried out under the conditions established [2] for the first of these. Dicarbonyl(4-methyl-nitrosobenzene)triphenylphosphineiron was prepared by refluxing for 3 h a solution of triphenylphosphine (1.5 g, 5.7 mmol) and bis[tricarbonyl(4-methyl-nitrosobenzene)iron] (0.3 g, 0.57 mmol) in ether (10 ml). The red precipitate was filtered off, washed with cold ether and air-dried to give the complex (0.43 g, 76%) m.p. 139–140 (dec). Found C, 64.4, H, 5.1, N, 2.8; $C_{27}H_{22}O_3NPFe$ requires C, 65.4, H, 4.4, N, 2.8. ν_{max} (KBr) 1991, 1940 cm^{-1}.

Solid state CPMAS ^{13}C NMR spectra were recorded at 75.431 MHz by the SERC service at the Industrial Research Laboratories, University of Durham using cross polarization (CP), magic angle spinning (MAS), and high power decoupling. All cross-polarization spectra were obtained with the Hartman-Hahn match condition fulfilled. The carbon secondary reference standard was adamantane CH_2 signal at 38.4 ppm relative to TMS. The data obtained are presented in Table 1.

Mössbauer spectra were obtained with samples cooled to 80 K and source at ambient temperature, in conventional transmission geometry, using a Harwell 6000 spectrometer and proportional detector. The spectra were fitted as Lorentzian doublets. The results are summarised in Table 2.

3. Discussion of Results

Previous work [2–4] implies that the $[Fe(CO)_3RNO]_2$ coordination complexes will be structurally similar and our Mössbauer spectrum for R = p-$CH_3C_6H_4$ is close to that reported by Frank and Bunbury [4] and the ^{13}C shifts for the CO groups are typical of terminal carbonyl groups and markedly different from those of bridging carbonyls [5]. The Mössbauer spectra for the two triphenylphosphine complexes are very similar to those for the dimeric complexes and this again suggests that all the compounds have related structures. The linewidths in our Mössbauer spectra are a little large due to the use of thick samples and the slight asymmetry of the spectra (which was also observed in the earlier work [4]) is probably caused by a degree of orientation of the crystallites during packing into the cell. In the dimeric complexes the iron atoms have an effective atomic number of eighteen. It thus seems probable that a terminal CO group in the bis[tricarbonyl(nitrosobenzene)iron] is replaced by a triphenylphosphine and that the resulting symmetrical solid complex is dimeric. There is as yet no means of establishing the mechanism of this displacement. It is possible that the dimeric complex dissociates into two molecules of monomer with this followed by a displacement of a CO group by triphenylphosphine and subsequent dimerisation. Alternatively displacement of two CO groups may take place from the dimer.

TABLE 2. Mössbauer data for nitrosoaromatic iron carbonyls at 80 K

Compound	Isomer shift [a] (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Width (mm s^{-1})
$[Fe(CO)_3.ptolNO]_2$ [b]	0.05	1.03	0.34, 0.40
$[Fe(PPh_3)(CO)_2 \cdot PhNO]_2$	0.09	1.02	0.31, 0.34
$[Fe(PPh_3)(CO)_2.ptolNO]_2$	0.08	0.99	0.32, 0.37

[a] Relative to metallic iron.

[b] ptol = p-$CH_3C_6H_4$.

The ^{13}C NMR spectra of the complexes are of particular interest in that they can afford evidence of structural changes in the ligand on coordination. This is facilitated by the fact that the NO group has a very large *ipso* substituent chemical shift (SCS) of 37.6 ppm [6]. Other double bonded nitrogen linked substituent

TABLE 1. Solid state ^{13}C NMR spectra of nitrosoaromatic iron carbonyls (values in ppm) [a]

Compound [b]	C1	C2	C3	C4	C5	C6	CH_3	CO	C1(PPh_3)
1	164.4	116.4	124.6	128.7	124.6	122.8		205.9[c], 202.9	
2	162.1	114.7	129.4	134.9	129.4	123.1	21.9	207.5, 205.4, 201.0	
3	162.0	117.2		132.9		117.2		215.8, 212.9	138.5, 129.2, 127.9
4	159.7	118.0		132.4		124.0	16.6	216.3, 214.4	131.3, 128.8

[a] Numbering of carbons in the nitrosoaromatic based upon the C2 being *syn* to the O of the NO group as employed for previous studies [8,9]. C3,5 for the triphenylphosphine complexes are obscured by the protonated carbons of the triphenylphosphine ligand.

[b] 1 = $[Fe(CO)_3(C_6H_5NO)]_2$; 2 = $[Fe(CO)_3(4\text{-}CH_3\text{–}C_6H_4NO)]_2$; 3 = $[Fe(CO)_2(PPh_3)(C_6H_5NO)]_2$; 4 = $[Fe(CO)_2(PPh_3)(4\text{-}CH_3\text{–}C_6H_4NO)]_2$.

[c] Intensity of this peak is much greater than for the other CO peak: probably corresponds to two CO groups.

groups have much smaller SCS values, *e.g.* NO_2, NCS, N=N(O)Ph, N(O)=NPh, N=NPh, N_2O_2Ph, N=CHR, for which the values lie in the range 3–30 ppm. Single bonded nitrogen linked substituent groups, such as NH_2, NR_2, and NHOR, have values of 22–26 ppm. The NO bond length in the example investigated by Barrow and Mills [1] is 1.40 Å, much closer to a single bond than to a double bond, and this is the result of type III coordination of the NO group [7], *i.e.* $\sigma N + \pi NO$, the lengthening of the NO bond being due to back donation from the iron d orbitals into the π^* NO orbitals. The drop in the C(1) shift is however only 2–3 ppm in the tricarbonyl complexes and 4–6 ppm in dicarbonyltriphenylphosphine complexes. We have shown elsewhere [8,9] that similar changes occur for type I (σ_N) and type VII (σ_O) coordination where the changes in the NO length and double bond character of the NO are very small in comparison. In only one example $PtCl_3$-(PhNO) [10] has an increase of the C(1) shift been observed on coordination.

Following the completion of our experimental work further evidence concerning the influence of type III coordination on the C(1) shifts in nitrosobenzene appeared [11]; in two complexes values of 157.9 and 158.3 ppm were observed, and in the first of these the NO length is 1.432 Å, in contrast, in a further example of a previously unknown coordination mode of a nitroso-compound (type VIII) (see Fig. 2) in which the NO π coordinates to two different rhodium atoms and the NO length is 1.422 Å, the C(1) resonance drops to 149.9 ppm, *i.e.* slightly lower than that found for N-phenylhydroxylamine [12]. We conclude that the NO bond lengthening to values characteristic of NO single bonds is, of itself, insufficient to induce large changes in the *ipso* chemical shift. Further examples of type VIII coordination are needed before we can conclude that double π coordination is the only mode of coordination of the NO group which produces substantial changes in the *ipso* chemical shift.

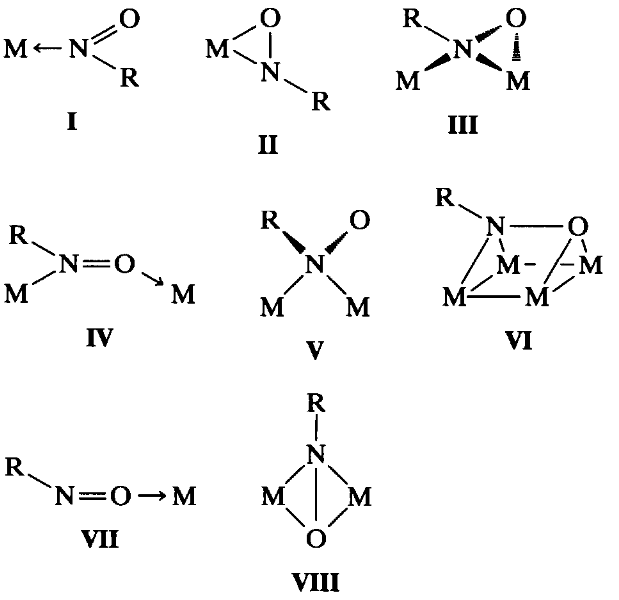

Fig. 2. The eight different coordination modes of monomeric C-nitrosocompounds to metals.

There is a further feature in the ^{13}C NMR spectra of substituted nitrosobenzenes to which we have drawn attention [8,9], namely the effect on the chemical shifts of the C(2) and C(6) atoms when the rotation of the NO group is 'frozen out' either in low temperature solution spectra or in solid state spectra. This effect is well established in the case of the free ligands [13–17] and is ascribed to the magnetic anisotropy of the NO group. It persists to a considerable extent in the coordination complexes of *p*-nitrosoanilines in which the coordination is σN or σO. In the case of the tricarbonyl complexes the values of $\Delta_{2,6}$ at -6.4 and -8.4 ppm are much smaller than those for the *p*-nitrosoaniline complexes [8,9] (ca $-19/-22$ ppm) and for 'frozen out' nitrosobenzene itself, at -34.5 ppm [13] the largest $\Delta_{2,6}$ value yet discovered for any functional group. Other examples of low $\Delta_{2,6}$ values are provided by CHO (-6.7) and OMe (-7.9ppm) [16]. It is possible, therefore, that type III coordination fundamentally alters the magnetic anisotropy of the NO group and/or that the NO group is no longer oriented in the plane of the aromatic ring.

Further insight into the effect of replacement of CO by PPh_3 is available both from the IR and ^{13}C NMR spectra. For the nitrosobenzene complexes the CO shifts increase by about 10 ppm and ν_{CO} decreases by about 70 cm^{-1}, whereas for the *p*-tolyl case the respective changes are about 9 ppm and 75 cm^{-1}.

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